[Document Name] Description

[Title of the Invention] Silicon system thin film photoelectrical conversion equipment

[Claim(s)]

[Claim 1] The back electrode, at least one silicon system photoelectrical conversion unit which have a substrate and a light reflex nature metal membrane, And while at least one of said light reflex nature metal membrane and said the front transparent electrodes has surface unevenness structure in the field by the side of a silicon system photoelectrical conversion unit and a concavo-convex vertical interval is in within the limits which is 0.01-2 micrometers including a front transparent electrode Silicon system thin film photoelectrical conversion equipment characterized by a concavo-convex pitch being within the limits of the 25 or less times more greatly than said vertical interval.

[Claim 2] While the field by the side of the silicon system photoelectrical conversion unit of said light reflex nature metal membrane has surface unevenness structure and a concavo-convex vertical interval is in within the limits which is 0.01-2 micrometers Silicon system thin film photoelectrical conversion equipment according to claim 1 characterized by a concavo-convex pitch being within the limits of the 25 or less times more greatly than said vertical interval.

[Claim 3] While the field by the side of the silicon system photoelectrical conversion unit of said front transparent electrode has surface unevenness structure and a concavo-convex vertical interval is in within the limits which is 0.01-2 micrometers Silicon system thin film photoelectrical conversion equipment according to claim 1 characterized by a concavo-convex pitch being within the limits of the

25 or less times more greatly than said vertical interval.

[Claim 4] While the field by the side of the silicon system photoelectrical conversion unit of both said light reflex nature metal membrane and said front transparent electrode has surface unevenness structure and a concavo-convex vertical interval is in within the limits which is 0.01-2 micrometers Silicon system thin film photoelectrical conversion equipment according to claim 1 characterized by a concavo-convex pitch being within the limits of the 25 or less times more greatly than said vertical interval.

[Claim 5] It is silicon system thin film photoelectrical conversion equipment given in either of 4 from Claim 1 characterized by the surface unevenness structure of the field by the side of the silicon system photoelectrical conversion unit of said light reflex nature metal membrane or said front transparent electrode being a curve which does not include a keen projection substantially.

[Claim 6] It is silicon system thin film photoelectrical conversion equipment given in either of 4 from Claim 1 characterized by the surface unevenness structure of the field by the side of the silicon system photoelectrical conversion unit of said light reflex nature metal membrane or said front transparent electrode being a curve which does not include a crooked point substantially.

[Claim 7] It is silicon system thin film photoelectrical conversion equipment given in either of 4 from Claim 1 characterized by said back electrode containing a transparent conductive oxide film in the silicon system photoelectrical conversion unit side.

[Claim 8] It is silicon system thin film photoelectrical conversion equipment given in either of 4 from Claim 1 characterized by at least one of said the photoelectrical conversion units containing 1 electric-conduction type layer, a crystalline material silicon system photoelectrical conversion layer, and a reverse electric conduction type layer.

[Claim 9] It is silicon system thin film photoelectrical conversion equipment given in either of 4 from Claim 1 characterized by the metal membrane in said back electrode having the high reflectance of 95% or more to the light of the wavelength within the limits of 500-1200nm.

[Claim 10] It is silicon system thin film photoelectrical conversion equipment given in either of 4 from Claim 1 characterized by forming the metal membrane in said back electrode with the alloy containing one or it which was chosen from Ag, Au, aluminum, and Cu and Pt.

[Claim 11] It is silicon system thin film photoelectrical conversion equipment according to claim 7 characterized by forming the interface with said transparent conductive oxide film among the metal membranes in said back electrode with the alloy containing one or it which was chosen from Ag, Au,

aluminum, and Cu and Pt.

[Claim 12] Said crystalline material silicon system photoelectrical conversion layer is formed under Shimoji temperature of 400 degrees C or less, and The rate of a volume crystallization part of 80% or more, The hydrogen content of 1 - 30 atom % within the limits, and the thickness within the limits of 0.5-20 micrometers, Silicon system thin film photoelectrical conversion equipment according to claim 8 which has a priority crystal orientation surface [being parallel to the film surface (110)], and is characterized by the intensity ratio of the diffraction peak to the diffraction peak (111) in the X diffraction (220) being 0.2 or less.

[Claim 13] Said silicon system photoelectrical conversion equipment is added to the crystalline material photoelectrical conversion unit containing said crystalline material silicon system photoelectrical conversion layer. Silicon system thin film photoelectrical conversion equipment according to claim 8 characterized by being the tandem type with which at least one of the amorphous photoelectrical conversion units containing an amorphous silicon system photoelectrical conversion layer was laminated.

[Claim 14] The back electrode and at least one silicon system photoelectrical conversion unit which have a light reflex nature metal membrane, and a front transparent electrode are silicon system thin film photoelectrical conversion equipment given in either of 13 from Claim 1 by which it is characterized [laminating in this order on a substrate, and].

[Detailed Description of the Invention]

[0001]

[Field of the Invention] Especially this invention relates to the reduction in cost and performance improvement of silicon system thin film photoelectrical conversion equipment about thin film photoelectrical conversion equipment.

[0002]

[Description of the Prior Art] Development of the photoelectrical conversion equipment using a silicon thin film, especially the thin film containing crystalline material silicon like polycrystalline silicon or micro crystallite silicon is performed energetically in recent years. These development is the trials in which the reduction in cost and highly-efficient-izing of photoelectrical conversion equipment will be reconciled by forming a good crystalline material silicon thin film in a low-temperature process on an inexpensive substrate, and the application to various pieces of photoelectrical conversion equipment,

such as not only a solar cell but a photosensor, is expected. In addition, in an application-concerned Description, the term of "many crystals", "micro crystallite", and "crystalline material" shall mean what contains the quality of amorphism partially as usually used in the technical field of thin film photoelectrical conversion equipment.

[0003] However, when a photoelectrical conversion layer is a thin film, sufficient absorption will not arise to the light of the long wavelength field where the optical absorption coefficient is small, but the photoelectrical converted quantity in a photoelectrical conversion layer will be restricted by the film thickness. In the case of the photoelectrical conversion layer containing especially crystalline material silicon, sufficient absorption is not produced. Since it is such, in order to use more effectively the light which entered into the photoelectrical conversion unit containing a photoelectrical conversion layer The device which carries out the dispersion reflection of the light into a photoelectrical conversion unit is made by preparing a metal layer with a high rate of a light reflex in the back side of a photoelectrical conversion unit, and preparing surface unevenness (surface texture) structure in this metal layer.

[0004] Moreover, surface unevenness (surface texture) structure is prepared also in the transparent electrode by the side of optical incidence, light is scattered into a photoelectrical conversion unit by it, and the device to which diffused reflection of the light further reflected with the metal electrode is carried out is also made. The photoelectrical conversion equipment containing the transparent electrode which has surface texture structure as mentioned above is indicated by JP,H6-12840,B, JP,H7-283432, A, etc., for example, and it is indicated that photoelectrical conversion efficiency improves.

[0005]

[Problem to be solved by the invention] By the way, a silicon system photoelectrical conversion unit which is typically used for the thin film polycrystalline silicon solar cell contains the photoelectrical conversion layer and conducted type layer of current which consist of a silicon system thin film. The conducted type layer of current by which impurities were doped causes reduction of the incidence light to a photoelectrical conversion layer by the optical absorption by the doped impurities. Therefore, in order to reduce the optical absorption by the impurities which are not contributed to such photoelectrical conversion and to increase the incidence light to a photoelectrical conversion layer, to make thin film thickness of the conducted type layer of current to necessary minimum is desired.

[0006] Under such a situation, [this invention persons] In order to increase the optical absorption in a photoelectrical conversion layer, when using the front transparent electrode and back electrode which have the surface unevenness structure which may produce desirable diffused reflection It found out that there was a problem that it is easy to produce a defect mechanical in the thin conducted type layer in the photoelectrical conversion unit which touches them of current, and electric, and it causes the fall of the yield by the fall and short circuit of open end voltage of a solar cell which are obtained.

[0007] In view of the technical problem in such a found-out prior art, by this invention persons, [this invention] It aims at aiming at an improvement of the photoelectric transfer characteristic by the optical confinement effect in the silicon system thin film photoelectrical conversion equipment formed only using a low-temperature process with an inexpensive usable substrate, without causing the fall of open end voltage, and the fall of the production yield.

[0008]

[Means for solving problem] The result of having repeated examination the above-mentioned technical problem which this invention persons found out being solved, In the silicon system thin film photoelectrical conversion equipment which forms all the semiconductor layers which constitute the semiconductor junction included in a photoelectrical conversion unit at low temperature with a plasma CVD method By controlling the concavo-convex vertical interval and concavo-convex pitch in the surface unevenness structure formed in the field by the side of the photoelectrical conversion unit of a back electrode or a front transparent electrode, it was found out that the highly efficient thin film photoelectrical conversion equipment with which high open end voltage can be obtained, and the amount of optical absorption in a photoelectrical conversion layer increases is obtained.

[0009] [namely, the silicon system thin film photoelectrical conversion equipment by this invention] The back electrode, at least one silicon system photoelectrical conversion unit which have a substrate and a light reflex nature metal membrane, And while either [at least] a light reflex nature metal membrane or a front transparent electrode has surface unevenness structure in the field by the side of a silicon system photoelectrical conversion unit and a concavo-convex vertical interval is in within the limits which is 0.01-2 micrometers including a front transparent electrode The concavo-convex pitch is characterized by being within the limits of the 25 or less times more greatly than a vertical interval. Here, the average value of the difference of the height of a convex part and a crevice is expressed, and the pitch expresses the mean distance between the adjoining convex parts, convex parts, or crevices as the vertical interval of surface unevenness.

[0010] While the field by the side of the silicon system photoelectrical conversion unit of a light reflex nature metal membrane has surface unevenness structure in this invention and a concavo-convex vertical interval is in within the limits which is 0.01-2 micrometers A concavo-convex pitch may be silicon system thin film photoelectrical conversion equipment characterized by being within the limits of the 25 or less times more greatly than said vertical interval.

[0011] Moreover, while the field by the side of the silicon system photoelectrical conversion unit of a front transparent electrode has surface unevenness structure and a concavo-convex vertical interval is in within the limits which is 0.01-2 micrometers A concavo-convex pitch may be silicon system thin film photoelectrical conversion equipment characterized by being within the limits of the 25 or less times

more greatly than said vertical interval.

[0012] While the field by the side of the silicon system photoelectrical conversion unit of both light reflex nature metal membrane and front transparent electrode has surface unevenness structure and these solar cells have a concavo-convex vertical interval in within the limits which is 0.01-2 micrometers A concavo-convex pitch may be silicon system thin film photoelectrical conversion equipment characterized by being within the limits of the 25 or less times more greatly than said vertical interval.

[0013] As for the surface unevenness structure of the field by the side of the silicon system photoelectrical conversion unit of a light reflex nature metal membrane or a front transparent electrode, it is desirable that it is the curve which does not include a keen projection substantially.

[0014] Moreover, as for the surface unevenness structure of the field by the side of the silicon system photoelectrical conversion unit of a light reflex nature metal membrane or a front transparent electrode, it is desirable that it is the curve which does not include a crooked point substantially. In addition, a crooked point means the point that inclination of a curve changes nonsequetially.

[0015] By the way, many pieces of the photoelectrical conversion equipment which made the silicon system photoelectrical conversion unit deposit on the back electrode containing a metal layer and transparent conductive oxide layers, such as a zinc oxide (ZnO) on it, is tried in recent years. for example, JP,3-99477,A; -- JP,7-263731,A; -- IEEE 1st World Conf.on Photovoltaic Energy Conversion -- [p.405(1994);Applied] It is reported in Physics Letters, Vol.70, p.2975 (1997), etc. Thus, by making a transparent conductive oxide layer intervene between the metal layer of a back electrode, and a silicon system photoelectrical conversion unit, the heat distortion by difference of the thermal expansion coefficient between them is eased, and a metal atom can prevent spreading and mixing into a silicon system photoelectrical conversion unit. As a result, it is known that the yield and reliability of photoelectrical conversion equipment which are acquired not only improve, but optical sensitivity will be improved and a photoelectric transfer characteristic will improve. Also in this invention, the transparent conductive oxide film may be contained in this way between the light reflex nature metal membrane and the silicon system photoelectrical conversion unit.

[0016] In this invention, when at least one of the photoelectrical conversion units contains 1 electric-conduction type layer, a crystalline material silicon system photoelectrical conversion layer, and a reverse electric conduction type layer, the effect of this invention is notably discovered.

[0017] As for a metal membrane, in the photoelectrical conversion equipment by this invention, it is desirable to have the high reflectance of 95% or more to the light of the wavelength within the limits of 500-1200nm.

[0018] As for a metal membrane, more specifically, it is desirable to be formed with the alloy containing one or it which was chosen from Ag, Au, aluminum, and Cu and Pt.

[0019] When the transparent conductive oxide film is contained between the light reflex nature metal membrane and the silicon system photoelectrical conversion unit, as for the interface with a transparent conductive oxide film, it is desirable among metal membranes to be formed with the alloy containing one or it which was chosen from Ag, Au, aluminum, and Cu and Pt.

[0020] When using a crystalline material silicon system photoelectrical conversion layer, it is formed under Shimoji temperature of 400 degrees C or less, and The rate of a volume crystallization part of 80% or more, It has the hydrogen content of 1 - 30 atom % within the limits, the thickness within the limits of 0.5-20 micrometers, and a priority crystal orientation surface [being parallel to the film surface (110)], and it is desirable that the intensity ratio of the diffraction peak to the diffraction peak (111) in the X diffraction (220) is 0.2 or less.

[0021] Moreover, in addition to the photoelectrical conversion unit containing a crystalline material silicon system photoelectrical conversion layer, the photoelectrical conversion equipment of this invention may be used as the tandem type with which at least one of the photoelectrical conversion units containing an amorphous silicon system photoelectrical conversion layer was laminated.

[0022] In the silicon system thin film photoelectrical conversion equipment by this invention, you may laminate on the substrate the back electrode and at least one silicon system photoelectrical conversion unit which have a light reflex nature metal membrane, and a front transparent electrode in this order.

[0023]

[Mode for carrying out the invention] With reference to the typical sectional view of drawing 1, the silicon system thin film photoelectrical conversion equipment by the form of operation of the 1st of this invention is explained. The inexpensive glass of metal, such as stainless steel, an organic film, Ceramics Sub-Division, or a low-melt point point etc. may be used for the substrate 1 of this photoelectrical conversion equipment.

[0024] As a back electrode 10 arranged on a substrate 1, the light reflex nature metal membrane 102 is formed. The compound layer which contains the light reflex nature metal membrane 102 and the transparent conductive oxide film 103 as a back electrode 10 is desirable. The light reflex nature metal membrane 102 can be formed on a substrate 1 by methods, such as vacuum deposition or weld slag. As for the reflexibility metal membrane 102, it is desirable to be formed with the alloy containing one or it which was chosen from Ag, Au, aluminum, and Cu and Pt. for example, the glass substrate 1 top -- the high Ag layer 102 of light reflex nature -- the substrate temperature within the limits of 100-330 degrees

C -- it can form by a vacuum deposition method under 200-300-degree C substrate temperature more preferably. Moreover, the adhesion between the glass substrate 1 and the Ag layer 102 can be raised by inserting the Ti layer 101 which has the thickness within the limits of 20-50nm between the glass substrate 1 and the Ag layer 102. In addition, such a Ti layer 101 can also be formed by vapor deposition or weld slag. As a transparent conductive oxide film 103, a zinc oxide is desirable.

[0025] The concavo-convex structure in the upper surface of the reflexibility metal membrane 102 can process the surface of a substrate 1 into a concavo-convex structure by etching etc. beforehand, and can obtain it by forming the thin metal membrane 102 which may transmit the concavo-convex structure to its own upper surface, for example. It is obtained also by instead forming the thin metal membrane 102 which may transmit that concavo-convex structure to its own upper surface, after depositing the transparent conductive oxide layer (not shown) which has the concavo-convex surface on a substrate 1.

[0026] While the vertical interval of the unevenness in the surface unevenness structure of the light reflex nature metal membrane 102 is within the limits of 0.01-2 micrometers, a concavo-convex pitch is larger than the vertical interval, and is 25 or less times. As for a concavo-convex vertical interval, 0.01-1micro are more desirable, 0.01-its 0.5micro are still more desirable, and 0.02-especially its 0.1micro are desirable. As for the concrete range of a concavo-convex pitch, it is desirable that it is in 0.3-1micro, and it is more desirable that it is in 0.5-0.8micro. Moreover, as for concavo-convex section form, it is desirable not to include a keen projection, and it is still more desirable not to include a crooked point substantially. In addition, such a surface unevenness structure may be measured by the surface observation by the TEM (transmission electron microscope) photograph and AFM (atomic force microscope) of a section of a metal membrane 102.

[0027] In the surface unevenness structure of the reflexibility metal membrane 102, if a concavo-convex vertical interval is too large to a pitch, the angle of a crevice and a convex part will become sharp. Formation of the semiconductor junction in the silicon system photoelectrical conversion unit deposited on it does not work, but causes the fall of the open end voltage of photoelectrical conversion equipment, or the manufacture yield finally obtained. That is, it was found out by the optimal value's existing about the concavo-convex vertical interval and concavo-convex pitch in the surface unevenness structure of the reflexibility metal membrane 102, giving the pitch of sufficient interval to a concavo-convex vertical interval, and making the angle of a crevice and a convex part loose that high open end voltage is obtained. Without being accompanied by the fall of open end voltage, or the fall of the manufacture yield by using the light reflex nature metal layer 102 which has the surface unevenness structure containing a vertical interval which is specified by this invention, and a pitch based on such knowledge, the optical confinement effect can be improved and highly efficient photoelectrical conversion equipment can be obtained.

[0028] As for the transparent conductive oxide film 103 formed on the light reflex nature metal membrane 102, it is desirable to be formed from at least one or more layers chosen from ITO, SnO_2, ZnO, etc., and especially its film that makes ZnO the main ingredients especially is desirable. As for the

diameter of an average crystal grain of the transparent conductive oxide film 103 which adjoins the photoelectrical conversion unit 11 and is arranged, it is desirable that it is 100nm or more, and in order to fill it, to form the transparent conductive oxide film 103 under the Shimoji temperature within the limits of 100-450 degrees C is desired. In addition, as for the film thickness of the transparent conductive oxide film 103 which makes ZnO the main ingredients, it is desirable that it is within the limits of 50nm - 1 micrometer, and, as for the specific resistance, it is desirable that it is below 1.5x10-3ohmcm.

[0029] On the back electrode 10, the silicon system photoelectrical conversion unit 11 is formed. All the semiconductor layers contained in this photoelectrical conversion unit 11 accumulate with a plasma CVD method under conditions with a Shimoji temperature of 400 degrees C or less. As a plasma CVD method, the parallel monotonous type RF plasma CVD generally known well can be used, and also frequency may use the plasma CVD using the high frequency power supply from RF belt of 150MHz or less to a VHF belt.

[0030] On the back electrode 10, 1 electric-conduction type layer 111 first contained in the photoelectrical conversion unit 11 accumulates. n type silicon system thin film by which the phosphorus which is a conducted type determination impurities atom of current, for example was doped as this 1 electric-conduction type layer 111, or p type silicon system thin film by which boron was doped may be used. However, these conditions about this 1 electric-conduction type layer 111 may not be restrictive, and nitrogen etc. is sufficient as them in n type layer as an impurities atom, for example. Moreover, as a material of 1 electric-conduction type layer 111, the silicon or its alloy material of many crystals or the micro crystallite which contains the quality of amorphism partially other than [other than amorphous silicon] alloy materials, such as amorphous silicon carbide and amorphous silicon germanium, can also be used. In addition, when wished, the carrier concentration by the rate of a crystallization part or the conducted type determination impurities atom of current can also be controlled by pulse laser irradiating such a deposited 1 electric-conduction type layer 111.

[0031] On 1 electric-conduction type layer 111, an amorphous silicon system thin film photoelectrical conversion layer or a crystalline material silicon system thin film photoelectrical conversion layer accumulates as a photoelectrical conversion layer 112. The silicon system thin film material which the polycrystalline silicon thin film of the intrinsic semiconductor of a non dope and the rate of a volume crystallization part fully equip with the photoelectrical conversion function as a crystalline material silicon system photoelectrical conversion layer 112 with 80% or more of micro crystallite silicone film, the weak p type containing a little impurities, or the weak n type may be used. However, this photoelectrical conversion layer 112 may not be limited to these, but may be formed using alloy materials, such as silicon carbide and silicon germanium.

[0032] The thickness of such a photoelectrical conversion layer 112 is within the limits of 0.1-20 micrometers. In the case of the amorphous silicon system thin film photoelectrical conversion layer 112, it is desirable that it is in the range the thickness of whose is 0.1-2 micrometers, and it is desirable that it

is in the range which is 0.15-0.5 micrometer. On the other hand, the range of required and sufficient film thickness as a crystalline material silicon system thin film photoelectrical conversion layer 112 is 0.5-20 micrometers. Moreover, since the crystalline material photoelectrical conversion layer 112 is formed at low temperature of 400 degrees C or less, the hydrogen content exists the defect in a crystal grain community or a grain within the limits of 1 - 30 atom %, including mostly a termination or the hydrogen atom made to inactivate. Furthermore, from the foundation layer, many of crystal grains contained in the crystalline material silicon system thin film photoelectrical conversion layer 112 are prolonged in the upper part pillar-shaped, and they have grown to be it. It has a priority crystal orientation surface [being parallel to the film surface (110)], and, as for the intensity ratio of the diffraction peak to the diffraction peak (111) in the X diffraction (220), it is desirable that it is 0.2 or less.

[0033] On the photoelectrical conversion layer 112, the silicon system thin film as a reverse type reverse electric conduction type layer 113 accumulates in 1 electric-conduction type layer 111. Although p type silicon system thin film by which boron which is a conducted type determination impurities atom of current, for example was doped as this reverse electric conduction type layer 113, or n type silicon system thin film by which the phosphorus was doped may be used, p type silicon system thin film is desirable. However, these conditions about this reverse electric conduction type layer 113 may not be restrictive, and aluminum etc. is sufficient as them in p type layer as an impurities atom, for example. Moreover, as a material of the reverse electric conduction type layer 113, alloy materials other than amorphous silicon, such as amorphous silicon carbide and amorphous silicon germanium, may be used, and the silicon or its alloy material of many crystals or the micro crystallite which contains the quality of amorphism partially can also be used.

[0034] Here, when the photoelectrical conversion unit 11 which the surface 1A of the back electrode 10 deposits on it even when substantially flat is a crystalline material photoelectrical conversion layer, surface texture structure including detailed unevenness is formed in the upper surface 1B. Moreover, when the upper surface 1A of the back electrode 10 has a concavo-convex texture structure, the pitch of the detailed unevenness in the texture structure of the upper surface 1B of the photoelectrical conversion unit 11 is small compared with it of the upper surface 1A of the back electrode 10. This is because the crystalline material photoelectrical conversion layer 112 contained in the photoelectrical conversion unit 11 produces a concavo-convex texture structure automatically at the time of the deposition, and [with this] The upper surface 1B of the photoelectrical conversion unit 11 becomes a detailed surface unevenness texture structure of having been suitable for scattering the incidence light of a wide range wavelength field, and the optical confinement effect in photoelectrical conversion equipment also becomes large.

[0035] It is ITO and SnO2 after lamination of the photoelectrical conversion unit 11 is completed. And the transparent conductive oxide film containing one or more layers chosen from ZnO is formed as a front transparent electrode 2. When the photoelectrical conversion unit 11 has surface unevenness structure, a concavo-convex structure according to the surface unevenness structure is formed in the field by the side of the photoelectrical conversion unit of the front transparent electrode 2. Moreover,

front transparent electrode 2 the very thing also has the tendency which produces a concavo-convex structure on the surface at the time of the film production. While the field by the side of the photoelectrical conversion unit of the front transparent electrode 2 also has a concavo-convex vertical interval in within the limits which is 0.01-2 micrometers, it is desirable that a concavo-convex pitch is within the limits of 25 or less times more greatly than the vertical interval.

[0036] In addition, in the form of operation of the 1st of this invention, if either or the both sides of the reflexibility metal membrane 102 or the front transparent electrode 2 has the vertical interval and pitch of the above-mentioned unevenness, the effect of this invention will be discovered. In the case of the thin film photoelectrical conversion equipment of drawing 1, when the reflexibility metal membrane 102 has the vertical interval and pitch of the above-mentioned unevenness, the effect of this invention is discovered most greatly. In this case, as for the front transparent electrode 2, it is desirable to have the vertical interval and pitch of the same unevenness as the reflexibility metal membrane 102, or to have a still more detailed concavo-convex structure.

[0037] Furthermore, the metal electrode of the shape of a comb type which contains the layer of at least one or more metal chosen from aluminum, Ag, Au, Cu, and Pt or these alloys as a grid electrode 3 on this front transparent electrode 2 is formed, and photoelectrical conversion equipment is completed. In such silicon system thin film photoelectrical conversion equipment, the light 4 by which photoelectrical conversion should be carried out is irradiated from the front transparent electrode 2 side.

[0038] Drawing 2 shows the silicon system thin film photoelectrical conversion equipment by the form of the 2nd operation which can replace the form of operation of the 1st of drawing 1. In addition, in drawing 1 and 2, the same reference number shows the portion which corresponds mutually. With the thin film photoelectrical conversion equipment of drawing 2, the front transparent electrode 2 is formed on the transparent substrates 1, such as glass. The light 4 by which photoelectrical conversion should be carried out enters from the transparent substrate 1 side. The transparent conductive oxide film containing one or more layers chosen from ITO, SnO2, and ZnO as a material of the front transparent electrode 2 is used, and it gets. Among such materials, from a viewpoint of transmissivity, an electric conduction rate, and chemical stability, especially SnO2 are suitable and they suitable also for ITO from a viewpoint of processability, an electric conduction rate, and transmissivity. The transparent electrode 2 may be formed on a substrate 1 by methods, such as vacuum deposition, Heat CVD, or weld slag. The silicon system thin film photoelectrical conversion unit 11 is formed on the front transparent electrode 2. The thing same as a photoelectrical conversion unit 11 as the photoelectrical conversion unit shown in drawing 1 may be used. As a conducted type layer 113 by the side of optical incidence of current, p type is desirable.

[0039] The light reflex nature metal membrane 102 is formed as a back electrode 10 on the photoelectrical conversion unit 11. However, as a back electrode 10, the composite membrane containing the light reflex nature metal membrane 102 and the transparent conductive oxide film 103 is desirable. That is, the back electrode's 10 also having been shown in drawing 1 and the same thing may

be used.

[0040] While in the case of the thin film photoelectrical conversion equipment of drawing 2 the front transparent electrode 2 has surface unevenness structure in the field by the side of the silicon system thin film photoelectrical conversion unit 11 and a concavo-convex vertical interval is in within the limits which is 0.01-2 micrometers When a concavo-convex pitch is within the limits of 25 or less times more greatly than the vertical interval, the effect of this invention is discovered most greatly. In this case, as for the reflexibility metal membrane 102, it is desirable to have the vertical interval and pitch of the same unevenness as the front transparent electrode 2, or to have a still more detailed concavo-convex structure.

[0041] Such a surface unevenness structure of a front transparent electrode forms a concavo-convex structure in the surface of a substrate 1 by etching etc., and forms the thin transparent electrode 2 on it. How to make the surface of the transparent electrode 2 a concavo-convex structure in alignment with a concavo-convex structure of the substrate 1, After depositing the transparent electrode layer which has the steep concavo-convex surface on a substrate 1, under a reduction atmosphere etc. Etching processing, It is obtained by the method of processing a desired loose concavo-convex structure by plasma polymerization, electron beam processing, corona treatment, etc., or the method of making the surface a loose concavo-convex structure by forming the layer which consists of other electric conduction layers, such as ZnO, on the lower layer which consists of SnO2 which have the steep concavo-convex surface.

[0042] For example, about 350 degrees C or more of temperature of the ground board 1 is first set as about 450-550 degrees C preferably, and the transparent electrode 2 which consists of SnO2 with the normal pressure heat CVD by using SnCl4, O2, CH3OH, HF, H2O, etc. as materials is formed. A surface concavo-convex structure can be adjusted to some extent by changing substrate temperature and the amount of introduction of each materials in the case of SnO2 (at for example, the time of the normal pressure heat CVD). Moreover, after vapor-depositing Zn layer on SnO two-layer, a desired loose concavo-convex structure can be acquired by etching using HCl etc. Under the present circumstances, surface unevenness structure can be adjusted by changing the amount of Zn vapor deposition and changing the amount of etching.

[0043] Next, with reference to the typical sectional view of drawing 3, the tandem type silicon system thin film photoelectrical conversion equipment by the form of operation of the 3rd of this invention is explained. In the tandem type photoelectrical conversion equipment of drawing 3, two or more layers 201-203 on a substrate 1, and 211-213 are similarly formed corresponding to two or more layers 101-103 on the substrate 1 of drawing 1, and 111-113.

[0044] However, in the tandem type photoelectrical conversion equipment of drawing 3, the 2nd unit 22 as a front photoelectrical conversion unit is formed further in piles on this using the 1st unit 21 which

contains a crystalline material silicon system photoelectrical conversion layer as a back photoelectrical conversion unit. [the 2nd photoelectrical conversion unit 22] The micro crystallite or the amorphous silicon system thin film 223 of the 1st electric conduction type micro crystallite deposited one by one with the plasma CVD method or the amorphous silicon system thin film 221, the amorphous silicon system thin film photoelectrical conversion layer 222 which is an intrinsic semiconductor substantially, and the reverse electric conduction type is included. On the 2nd photoelectrical conversion unit 22, it is formed like the case where the front transparent electrode 2 and the comb type metal electrode 3 are drawing 1, and tandem type photoelectrical conversion equipment as is shown to drawing 3 by this is completed.

[0045] Drawing 4 shows the tandem type photoelectrical conversion equipment by the form of the 4th operation which can replace the form of operation of the 3rd of drawing 3. The relation between drawing 3 and the photoelectrical conversion equipment of 4 is similar to drawing 1 and the relation of 2, and the same reference number in drawing 3 and 4 expresses the portion which corresponds mutually.

[0046] In the following, the silicon system thin film photoelectrical conversion equipment by some work examples of this invention is explained with the photoelectrical conversion equipment by a comparative example.

[0047] (Work example 1) Corresponding to the form of the 1st operation explained with reference to drawing 1, silicon system thin film photoelectrical conversion equipment was produced as a work example 1. In this work example 1, the back electrode 10 was formed on the glass substrate 1. The back electrode 10 contains the Ti layer 101 with a thickness of 20nm deposited one by one, the 300-nm-thick Ag layer 102, and the 100-nm-thick ZnO layer 103. The Ag layer 102 which works as a light reflex nature metal membrane was deposited by vacuum deposition among these. On the back electrode 10, n type layer 111 contained in the silicon system thin film photoelectrical conversion unit 11, the crystalline material silicon system photoelectrical conversion layer 112 of a non dope, and p type layer 113 were formed by the plasma CVD method. Moreover, as a front electrode 2 on the photoelectrical conversion unit 11, the 80-nm-thick transparent conductive ITO film was formed, and the comb type Ag electrode 3 for current extraction was formed on it.

[0048] Depositing the crystalline material silicon system photoelectrical conversion layer 112 of the non dope included in the photoelectrical conversion unit 11 with RF plasma CVD method under 300-degree C Shimoji temperature, the film thickness was 1.5 micrometers. In this crystalline material photoelectrical conversion layer 112, the hydrogen content calculated by secondary ion mass spectrometry was 2.3 atom %, and the intensity ratio of the diffraction peak to the diffraction peak (111) in an X diffraction (220) was 0.084.

[0049] In the output characteristic when irradiating the photoelectrical conversion equipment by such a work example 1 with the light volume of 100 mW/cm2 as an incidence light 4 of AM1.5, 22.5mA/cm2

and the curvilinear factor of 0.550V and short-circuit current density were [open end voltage / 76.8% and conversion efficiency] 9.50%.

[0050] In work examples 2-5 and comparative examples 1-2 (Work examples 2-5 and comparative examples 1-2) silicon system thin film photoelectrical conversion equipment was produced under the same method as a work example 1, and conditions except the surface unevenness state having boiled many things, and having been changed by changing the Shimoji temperature and vapor deposition speed at the time of forming the Ag layer 102 which is a light reflex nature metal thin film. The vertical interval, the pitch and the pitch / vertical interval of the unevenness in the surface unevenness structure of the obtained Ag layer 102 are shown in Table 1 with the various photoelectric transfer characteristics of photoelectrical conversion equipment. In addition, in Table 1, the result related with a work example 1 is also shown.

[0051]

[Table 1]

[0052] The optical absorption characteristic in the photoelectrical conversion equipment by work examples 1-3 is shown by the graph of drawing 5. That is, in this graph, a horizontal axis expresses the wavelength of light and the vertical axis expresses the external quantum efficiency of photoelectrical conversion equipment. Moreover, the curve A of a solid line, the curve B of a dotted line, and the curve C of the one-point chain line express the spectral sensitivity characteristic in the photoelectrical conversion equipment by work examples 1, 2, and 3, respectively. In addition, also in which the work example and comparative example, it was set as 1.5 micrometers whose thickness of the crystalline material photoelectrical conversion layer 112 is comparatively thin in order to make it easy to enlarge influence of the optical confinement effect in a 600-1000nm long wavelength field, and to check.

[0053] , so that I may be understood from the graph of Table 1 and drawing 5 and the ratio of the pitch/ vertical interval in surface unevenness of the Ag layer 102 becomes small That is, the external quantum efficiency in a 600-1000nm long wavelength field is high, so that surface unevenness becomes intense, and this means that the optical confinement effect is increasing.

[0054] On the other hand, the open end voltage shown in Table 1 is not necessarily in agreement with the tendency of the spectral sensitivity characteristic shown in drawing 5, and the value whose ratio of the pitch/vertical interval in surface unevenness of the Ag layer 102 is comparatively high at about ten to 20 within the limits is shown.

[0055] By the way, the case where the ratio of the pitch/vertical interval in surface unevenness of the Ag layer 102 is extremely small, and the case of being large are shown by comparative examples 1 and 2, respectively. Also in these comparative examples, the direction of the comparative example 2 including more gently-sloping surface unevenness shows the high open end voltage value. However, according to the measurement result of the spectral sensitivity characteristic same with being shown in drawing 5, in the direction of the comparative example 2, compared with the comparative example 1, the optical confinement effect was low. Moreover, although the cause was not clear, even if the surface unevenness state was too intense like a comparative example 1, the result that the optical confinement effect became low on the contrary compared with a work example was obtained.

[0056] As mentioned above, [since the surface of the metal thin film 102 which reflects light shuts up light in the photoelectrical conversion unit 11, to have a concavo-convex structure to some extent is desired, but] Formation of the semiconductor junction in the photoelectrical conversion unit 11 which the vertical interval of the unevenness is too large, and will be formed on it if the angle of a crevice and a convex part becomes sharp will not work, but will cause the fall of the open end voltage of photoelectrical conversion equipment, or the manufacture yield. Since it is such, it turns out that the suitable range exists in the parameter of a surface unevenness state of the light reflex nature metal membrane 102. That is, the surface unevenness state has a vertical interval within the limits of 0.01-2 micrometers, and the ratio of concavo-convex pitch/vertical interval is larger than 1 time, it is desirable that they are 25 or less times, and it is more desirable that it is within the limits of four to 20 times.

[0057] (Work example 6) Corresponding to the form of operation of the 3rd of this invention explained with reference to drawing 3, tandem type photoelectrical conversion equipment was produced as a work example 6. In the tandem type photoelectrical conversion equipment of this work example 7, the elements 201-203 on the glass substrate 1, and 211-213 were formed like the elements 101-103 with which a work example 1 corresponds, and 111-113. However, the film thickness of the crystalline material silicon system photoelectrical conversion layer 212 was set as a thickness of 3.0 micrometers. On the 1st unit 21 as a back photoelectrical conversion unit, the 2nd unit 22 as a front photoelectrical conversion unit was laminated further. This 2nd photoelectrical conversion unit 22 contains n type layer 221 laminated one by one, the amorphous silicon system photoelectrical conversion layer 222, and p type layer 223. The thickness of the amorphous photoelectrical conversion layer 222 was set as 300nm. On the 2nd photoelectrical conversion unit 22, the front electrode 2 of transparent and the comb type Ag electrode 3 were formed like the case of a work example 1.

[0058] As an output characteristic when glaring the light of AM1.5 with the light volume two of 100mW/cm as an incidence light 4 to the tandem type silicon system thin film photoelectrical conversion equipment of amorphous / crystalline material type by such a work example 6 13.0mA/cm2 and the curvilinear factor of 1.42V and short-circuit current density were [open end voltage / 73.5% and conversion efficiency] 13.6%.

[0059] As mentioned above, according to this invention, the silicon system thin film photoelectrical

conversion equipment which combines the high optical confinement effect and high open end voltage can be offered, and it can contribute to the reduction in cost and highly-efficient-izing of silicon system thin film photoelectrical conversion equipment greatly.

[Brief Description of the Drawings]

[Drawing 1] It is a typical sectional view for explaining the silicon system thin film photoelectrical conversion equipment by the form of operation of the 1st of this invention.

[Drawing 2] It is a typical sectional view for explaining the silicon system thin film photoelectrical conversion equipment by the form of operation of the 2nd of this invention.

[Drawing 3] It is a typical sectional view for explaining the tandem type silicon system thin film photoelectrical conversion equipment of amorphous / crystalline material type by the form of operation of the 3rd of this invention.

[Drawing 4] It is a typical sectional view for explaining the tandem type silicon system thin film photoelectrical conversion equipment of amorphous / crystalline material type by the form of operation of the 4th of this invention.

[Drawing 5] It is the graph which shows the light wavelength dependability of the external quantum efficiency in some photoelectrical conversion equipment by the work example of this invention.

[Explanations of letters or numerals] 1: Substrate, such as glass, 2: Transparent conductive oxide film 3: Comb type metal electrode 4: Illuminating radiation 10, 20: The back electrode 11, 21: Crystalline material silicon system photoelectrical conversion unit 22: The amorphous silicon system photoelectrical conversion unit 101, 201: The transparent conductive oxide films 111 and 211, such as the metal membranes 103, such as the metal membranes 102, such as Ti, and 202:Ag, and 203:ZnO, the 221:1 electric-conduction type layer 112, the 212:crystalline material silicon system photoelectrical conversion layer 222 : The amorphous silicon system photoelectrical conversion layers 113 and 213, the 223:reverse electric conduction type layer 1A, 2A: The upper surfaces 1B and 2B of a ground electrode : the upper surface of a crystalline material silicon system photoelectrical conversion unit

[Translation done.]